ARMY RESEARCH LABORATORY

Infrared Techniques for Studying Coating Durability and Performance

William S. Lum
Philip H. Patterson

ARL-MR-319 July 1996

NOTICES

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	July 1996	Progress, November 1994 - September 1995

4. TITLE AND SUBTITLE

Infrared Techniques for Studying Coating Durability and Performance

5. FUNDING NUMBERS

5S2HDL

6. AUTHOR(S)

William S. Lum and Philip H. Patterson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Research Laboratory
ATTN: AMSRL-MA-PE
Fort Belvoir, VA 22060-5812

8. PERFORMING ORGANIZATION REPORT NUMBER

ARL-MR-319

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

10.SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

POC: William S. Lum, DSN 654-2801 or COM (703) 704-2801

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

This interim report describes the progress of the first stage of this 2-year ARL project. Determining possible infrared characterization techniques to be used in a progressive study of chemical-agent-resistant coating (CARC) materials was the main effort, using a Fourier transform infrared (FT-IR) instrument. Attenuated total reflectance (ATR) technology and other techniques were applied to analyze samples accurately, easily, and cost effectively. Preliminary results show that benefits can be realized in durability studies and weatherability determination of materials.

14. SUBJECT TERMS

chemical-agent-resistant coatings (CARC), Fourier transform infrared (FT-IR), weatherability, durability study, materials

15. NUMBER OF PAGES

14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

INTENTIONALLY LEFT BLANK.

TABLE OF CONTENTS

INTENTIONALLY LEFT BLANK.

LIST OF FIGURES

INTENTIONALLY LEFT BLANK.

1. BACKGROUND

The first part of this 2-year investigation utilized advanced instrumentation and sampling accessories. The main thrust was to determine possible infrared (IR) characterization techniques to be used in a progressive study of chemical-agent-resistant coating (CARC) materials.

The current physical degradation or durability studies are not only time-consuming, but they also produce poor correlation between both Q-Ultra Violet (Q-UV, Q-Panel Lab Products, Cleveland, OH) and Atlas Xenon-Arc (Atlas Electric Devices Company, Chicago, IL) accelerated weathering tests vs. Florida exposure tests. Additionally, they suffer from data scattering.

Benefits realized from this study may include effective techniques for further research, increased knowledge of CARC coatings in relation to chemical and physical degradation, and a greater understanding of chemical changes occurring during the weathering process.

There is an apparent need to shorten the time it takes to determine the weatherability of materials. The objective of this study is to determine a possible technique or techniques that are less time-consuming, effective, and capable of being performed by a spectroscopist with limited coatings experience.

2. APPROACH

The Fourier transform infrared (FT-IR) spectrometer (Model 5DX-B, Nicolet Instrument, Madison, WI) was used to investigate the various sampling techniques. The instrument was also used to run existing coating samples and newly formulated coating materials.

The accessories and techniques identified and selected for this study were as follows:

(1) magnetic sample holders with electronic grade silicon wafers (Harrick Scientific Corp.),
(2) polyethylene screen cells (Janos Technology, Inc.),
(3) 3M disposable IR cards, both polyethylene (PE) and polytetrafluroethylene (PTFE) substrates (3M New Products Development, Inc.),
(4) vertical attenuated total reflectance (ATR), and
(5) free films via transmittance.

The study began by reviewing application literature on FT-IR accessories and sampling methods. Technical training on weathering techniques and IR interpretation was obtained, followed by procurement of supplies, accessories, and related equipment.

Preliminary coating samples were run on a trial basis using different spectroscopic techniques and accessories. A spectrum of each sample, before and after outdoor exposure and accelerated weathering methods, was scanned and saved in the software's spectrum file or the .SPA extension as a standard procedure. This report covers all the initial findings in the Results and Conclusions sections.

In the latter part of the study, specific IR absorption bands will be monitored to follow the chemical degradation process. The same outdoor exposure and accelerated weathering techniques will be used for all samples. Techniques will be fine-tuned as problems arise from trial runs. Changes will be made to optimize the FT-IR instrument and sample film preparation for the best reproducibility.

The final objective is to determine the most efficient technique for evaluating coating materials based on their weathering properties. A technical report will conclude the entire investigation by encompassing all the results of the analysis. Furthermore, development of a technology base to enhance and reinforce any spin-off studies may result from this investigative research.

3. EXPERIMENTAL

Coated and uncoated silicon wafer magnetic holders, screen cells, and disposable IR cards underwent both natural and accelerated weathering. The applied coating consisted of a clear two-component polyester polyurethane. The resins, Desmophen 650A-65 polyester polyol and Desmodur N-75 polyisocyanate, were obtained from Bayer Chemicals, Inc., Pittsburgh, PA.

The natural weathering phase was performed at Fort Belvoir, VA, with the racks facing in a southerly direction at a 45° angle. This procedure follows the requirements as specified by the U.S. Army Research Laboratory's (ARL) CARC specifications.

OMNIC, the FT-IR software that was used, was employed to acquire background and sample spectra, peak positions, and tables. OMNIC is unique in the sense that it is for Nicolet's instruments only. Initially, version 1.1 was installed in the computer. However, an updated 2.0 version became available and was implemented for use in most parts of this project.

A new background was used for each sample. Transmittance was converted into absorbance in order to do a baseline correction. The appearances of the spectra were adjusted using baseline corrections and data smoothing.

Thallium bromoiodide (KRS-5) crystal was used with a vertical ATR (Spectra-Tech, Inc. Stamford, CT). The spectral range of the crystal is from 2,200 cm^{-1} to 250 cm^{-1}, which allows an extended view of the lower region of the spectrum. The resolution was set at 4 cm^{-1}. Spectra were measured in the range of 4,000 cm^{-1} to 400 cm^{-1}.

A concept that was derived and tried involved the preparation and analysis of free-standing strips of cured films. The free-film concept was somewhat effective; however, it proved to be extremely sensitive to film thickness and very difficult to reproduce quality spectra.

4. RESULTS

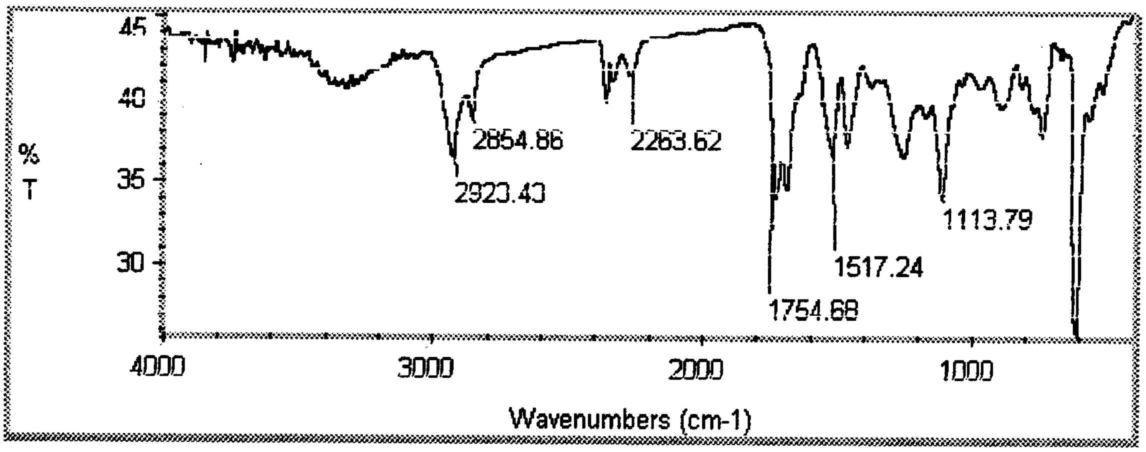
A particular band was used for each analysis. In the case of CARC coatings, the band was approximately 2,265 cm^{-1}, which signifies a presence of unreacted isocyanate. Based on the curing time, the intensity shows the completeness of the polyurethane reaction (polyisocyanate with chain-terminating polyol). This band was used to monitor the chemical change that was occurring, such as the completeness of reaction.

Figure 1a is a spectrum of Bayer 650A-65 cured with Bayer N-75 before any exposure was done to the film. Note the band at 2,263 cm^{-1}. A peak table is compiled below the spectrum.

Figure 1b shows the result of the same material after 1 month of natural exposure. We labeled a diminishing band at 2,260 cm^{-1} on the spectrum.

Silicon wafers with a magnetic holder became the best technique by far out of the possible three. Figure 2 is a spectrum demonstrating that we can track the isocyanate band. This shows that we can track any band representing chemical change. Note the disappearance of the same band at 2,267 cm^{-1}. Figures 3–5 show how extensive the deterioration can be on these screen cells and IR cards. Therefore, they will not be used in any future studies.

Tues July 11 10:36:02 1995
Collect Sample:
Spectrum Title: Thur Mar 09 14:48:02 1995
Resolution: 4.000cm-1
Number of scans: 50
A new background spectrum was collected.
A new sample spectrum was collected.
Silicon wafer in a Harrick magnetic holder
Bayer 650A-65 and N-75
C:\omnic\log\harrick.log
harrick.log, log file
before natural exposure
Spectrum, Figure 1-A

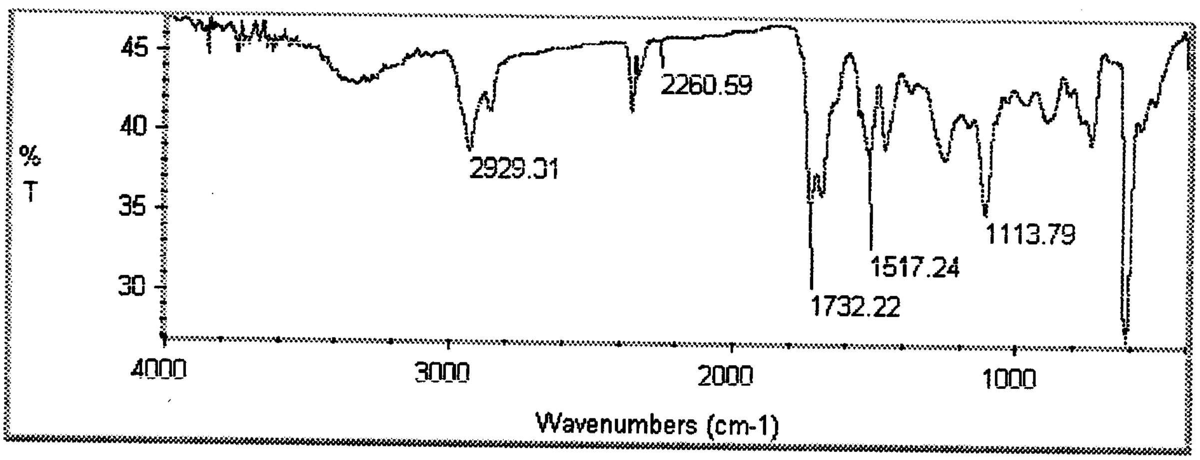


Tue Jul 11 15:19:52 1995
FIND PEAKS:
Spectrum: **Thu Mar 09 14:48:02 1995
Region: 4000.00 400.00
Absolute threshold: 36.545
Sensitivity: 50
Peak list:

Position: 612.43	Intensity: 25.831
Position: 616.49	Intensity: 26.094
Position: 1111.54	Intensity: 34.053
Position: 1256.33	Intensity: 36.389
Position: 1689.39	Intensity: 34.462
Position: 1731.11	Intensity: 33.912
Position: 2931.23	Intensity: 36.541

Figure 1a. FT-IR spectrum of resins before natural exposure.

Tues July 11 10:27:53 1995
Collect Sample:
Spectrum Title: Thu Apr 06 13:36:31 1995
Resolution: 4.000cm-1
Number of scans: 50
A new background spectrum was collected.
A new sample spectrum was collected.
Silicon wafer in a Harrick magnetic holder
Bayer 650A-65 and N-75
C:\omnic\log\harrick1.log
harrick1.log, log file
after natural exposure, 1 month
Spectrum, Figure 1-B

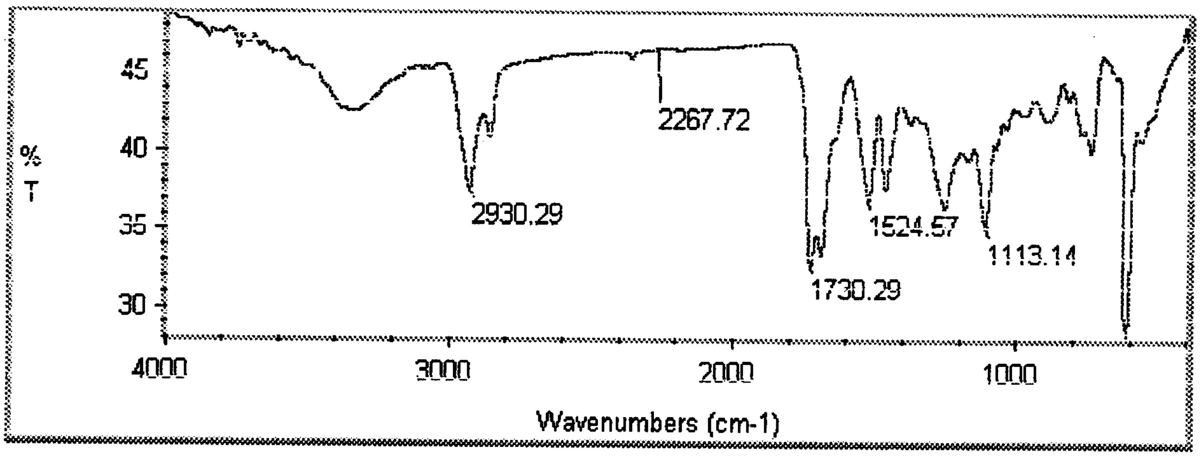


Tue Jul 11 14:23:05 1995
FIND PEAKS:
Spectrum: **Thu Apr 06 13:36:31 1995
Region: 4000.00 400.00
Absolute threshold: 39.022
Sensitivity: 50
Peak list:

Position: 612.89	Intensity: 26.874
Position: 1111.65	Intensity: 35.232
Position: 1257.14	Intensity: 38.251
Position: 1523.60	Intensity: 38.725
Position: 1690.67	Intensity: 36.139
Position: 1726.34	Intensity: 35.670
Position: 2931.88	Intensity: 38.873

Figure 1b. FT-IR spectrum of resins after 1 month of natural exposure.

```
Mon July 10 10:10:08 1995
Collect Sample:
      Spectrum Title: Thu May 04 14:04:21 1995
      Resolution: 4.000cm-1
      Number of scans: 50
      A new background spectrum was collected.
      A new sample spectrum was collected.
      Silicon wafer in a Harrick magnetic holder
      Bayer 650A-65 and N-75
      C:\omnic\log\harrick2.log
      harrick2.log, log file
      after natural exposure, 2 months
      Spectrum, Figure 2
```




```
Tue Jul 11 10:10:10 1995
FIND PEAKS:
       Spectrum:  **Thu May 04 14:04:21 1995
       Region:    4000.00        400.00
       Absolute threshold:   37.294
       Sensitivity:     50
       Peak list:
             Position:  610.18       Intensity: 27.736
             Position:  1112.58      Intensity: 34.935
             Position:  1255.32      Intensity: 36.218
             Position:  1463.61      Intensity: 37.281
             Position:  1523.25      Intensity: 36.732
             Position:  1688.19      Intensity: 32.974
             Position:  1727.47      Intensity: 32.498
             Position:  2932.29      Intensity: 37.266
```

Figure 2. <u>FT-IR spectrum of resins after 2 months of natural exposure</u>.

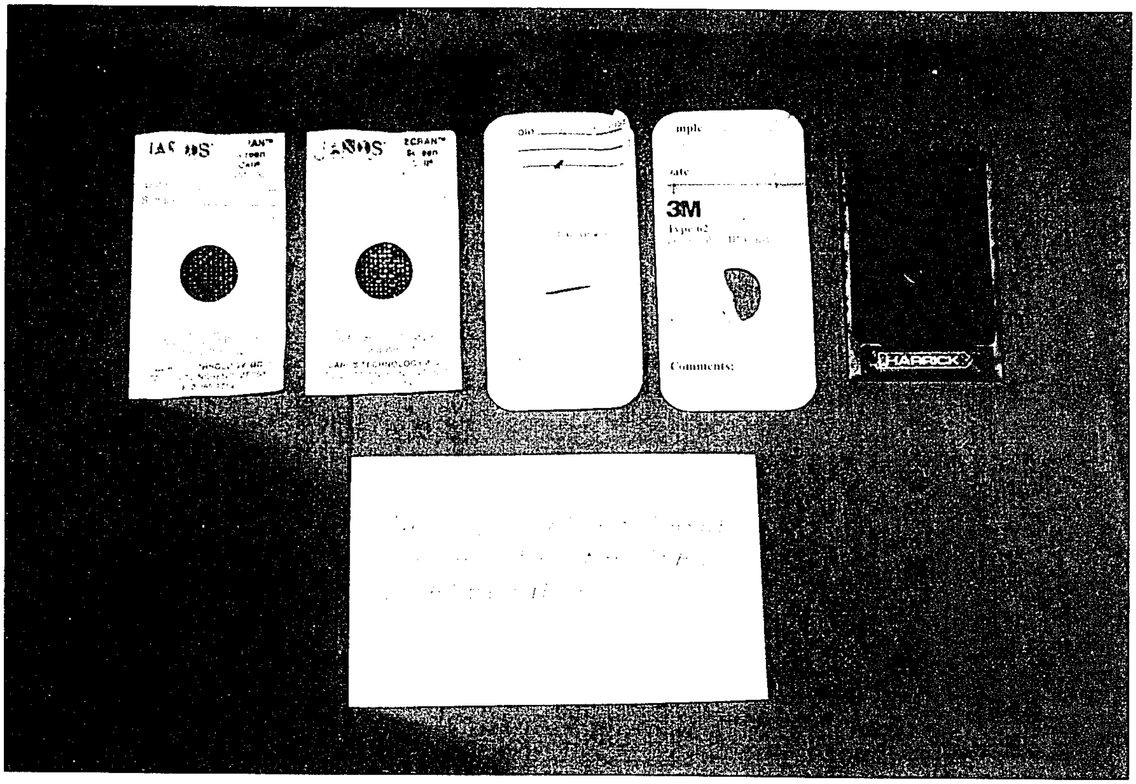


Figure 3. Samples after 3 months of natural weathering.

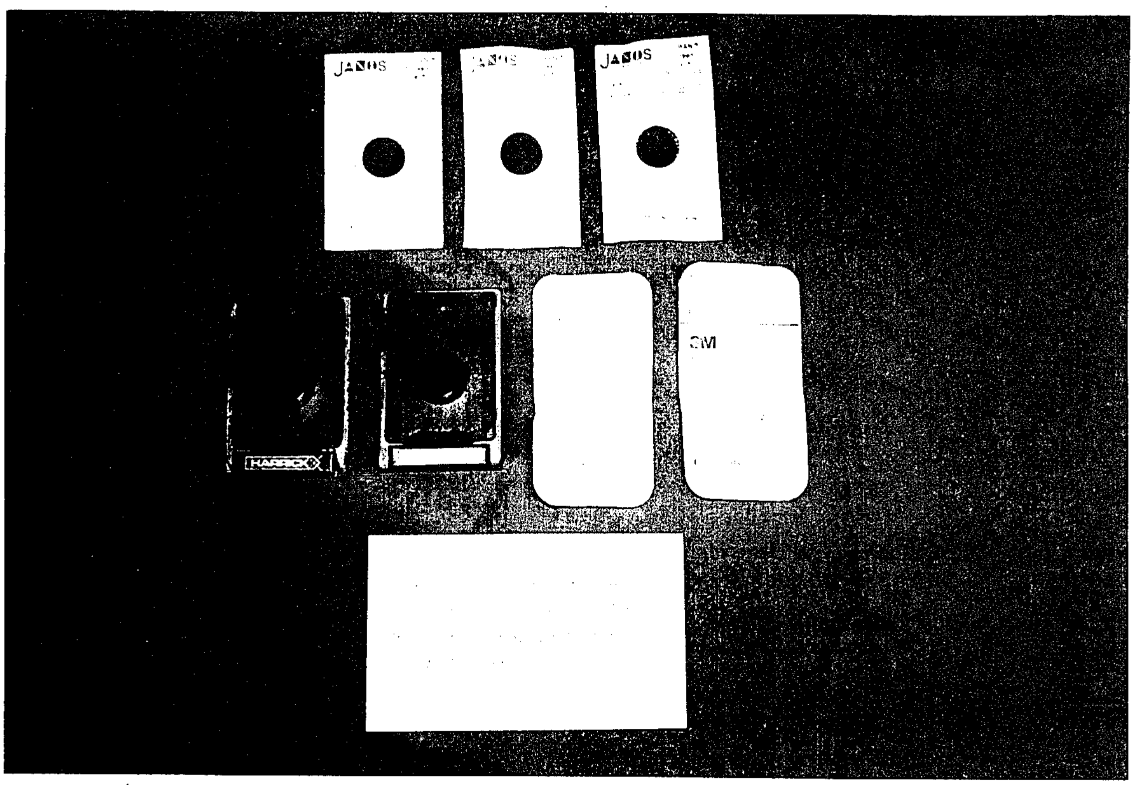


Figure 4. Samples after 360 hr of Xenon-Arc exposure.

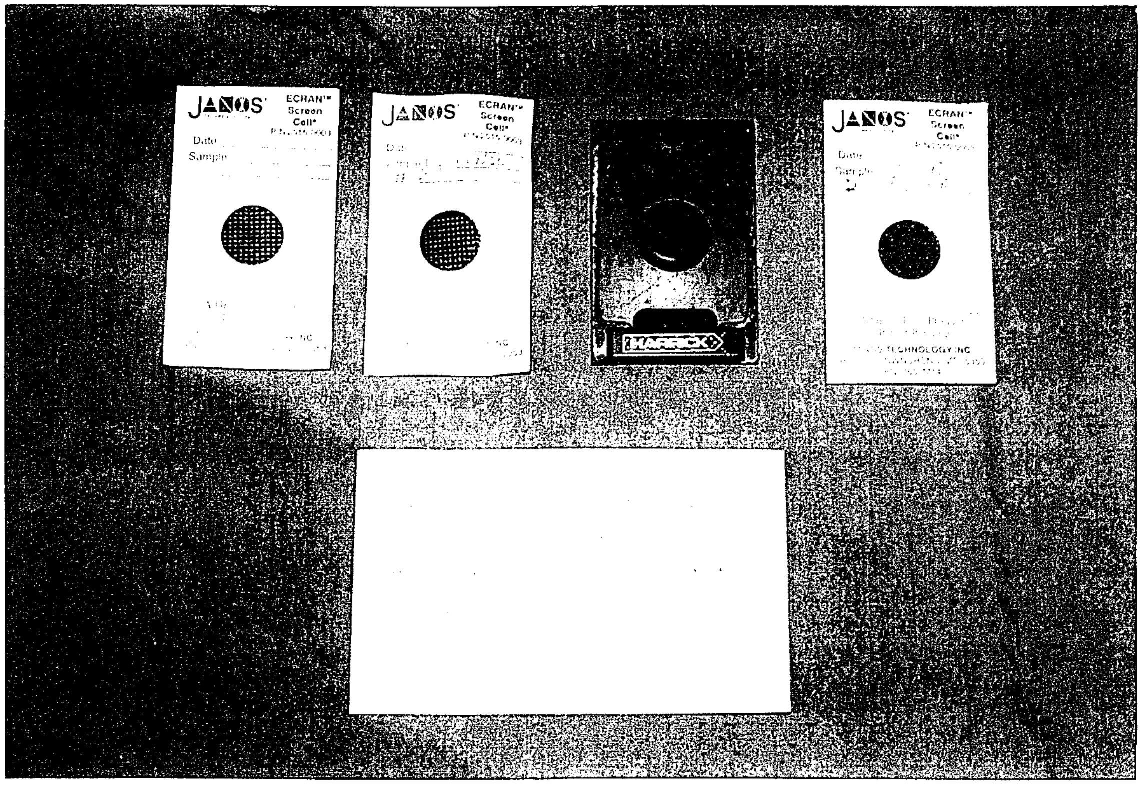


Figure 5. Samples after 400 hr of QUV exposure.

5. CONCLUSIONS

A practical approach in studying CARC materials is using a silicon wafer in a magnetic holder. We have found that using silicon wafer is the best way in tracking particular spectral bands relating to chemical degradation process. However, this approach has a higher start-up cost than the disposable cards. Most projects have to be within budget; therefore, cost is an important consideration.

Once the equipment are ready to run, the silicon wafer approach should take only minutes to analyze the sample. This method allowed the authors to turnaround the samples quickly into testing again for another cycle of exposure. It is proven to be less time-consuming, effective, and easily done.

6. PLANS

Additional work on this project will continue into next year. A final publication with recommendations and significant findings will complete this study at the end of fiscal year 1996 (FY96).

Plans for future work include the following:

(1) troubleshooting the trial runs,

(2) configuring and maximizing the FT-IR instrument and its accessories,

(3) compiling and analyzing the results, and

(4) finalizing a technical report.

INTENTIONALLY LEFT BLANK.

NO. OF COPIES	ORGANIZATION
2	DEFENSE TECHNICAL INFO CTR ATTN DTIC DDA 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL OP SD TA 2800 POWDER MILL RD ADELPHI MD 20783-1145
3	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL OP SD TL 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL OP SD TP 2800 POWDER MILL RD ADELPHI MD 20783-1145
	ABERDEEN PROVING GROUND
2	DIR USARL ATTN AMSRL OP AP L (305)

NO. OF COPIES	ORGANIZATION
2	COMMANDER US ARMY MATERIEL COMMAND ATTN AMCCE Q AMCDMA ML 5001 EISENHOWER AVE ALEXANDRIA VA 22333-0001
2	COMMANDER US ARMY NATICK RD&E CENTER ATTN STRNC EP STRNC ML NATICK MA 01760-5014
1	COMMANDER US ARMY FRGN SCI & TECHLGY CTR ATTN AMCST IS3 220 7TH STREET NE CHARLOTTESVILLE VA 22901-5396
1	COMMANDER US ARMY CORPS OF ENGINEERS ATTN DAEN ASI TECH LIB 20 MASSACHUSETTS AVE NW ROOM 3119 WASHINGTON DC 20314
1	COMMANDER NAVAL AIR SYSTEMS COMMAND ATTN TECH LIB AIR 00D4 WASHINGTON DC 20361
1	COMMANDER NAVAL SEA SYSTEMS COMMAND LBRY DOCUMENTATION BRANCH SEA 9661 WASHINGTON DC 20362
1	ARMY RESEARCH LABORATORY ATTN AMSRL CC OFC OF THE CHIEF COUNSEL 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	ARMY RESEARCH LABORATORY ATTN AMSRL AS ADMIN SUPPORT OFC 2800 POWDER MILL RD ADELPHI MD 20783-1197

NO. OF COPIES	ORGANIZATION
1	DIRECTOR NAVAL RESEARCH LABORATORY ATTN TECH LIB WASHINGTON DC 20375
10	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL MA PE FT BELVOIR VA 22060-5812
	ABERDEEN PROVING GROUND
4	DIR, USARL ATTN: AMSRL-MA
1	DIR, USA ERDEC ATTN: AMSMC-QAV

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number/Author ARL-MR-319 (Lum) ____ Date of Report July 1996 ____

2. Date Report Received ____

3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) ____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) ____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. ____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) ____

CURRENT ADDRESS

Organization ____

Name ____

Street or P.O. Box No. ____

City, State, Zip Code ____

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

OLD ADDRESS

Organization ____

Name ____

Street or P.O. Box No. ____

City, State, Zip Code ____

(Remove this sheet, fold as indicated, tape closed, and mail.)
(DO NOT STAPLE)

DEPARTMENT OF THE ARMY

OFFICIAL BUSINESS

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL
FIRST CLASS PERMIT NO 0001,APG,MD

POSTAGE WILL BE PAID BY ADDRESSEE

DIRECTOR
U.S. ARMY RESEARCH LABORATORY
ATTN: AMSRL-MA-PE
FT BELVOIR VA 22060-5606